Liquid Crystal Transitions

ChemPubSoc

An Unusual Stacking Transformation in Liquid-Crystalline **Columnar Assemblies of Clicked Molecular Propellers with Tunable Light Emissions**

Jinhee Kim,^[a] Sung Cho,^[b] and Byoung-Ki Cho^{*[a]}

Abstract: The columnar liquid-crystalline (LC) and fluorescence properties of three-dimensional molecular propellers based on tetraphenylethylene is reported. X-ray scattering studies reveal an unusual transition from a rectangular (Col_{rec}) to a hexagonal columnar (Col_{hex}) phase. In contrast to second-order intercolumnar transitions based on a common tilt mechanism, the transition is first order and involves an unprecedented zigzag stacking of aromatic propellers in the Col_{rec} phase. A sudden change in emission color from sky blue to green occurs rapidly and reversibly at this transition, which is due to the planarization of the propeller mesogen.

Columnar liquid crystal (LC) assemblies are an attractive research field because they can provide an anisotropic onedimensional (1D) conducting channel for electrons, holes, and photons through the $\pi\text{-}overlap$ of neighboring aromatic cores.^[1] The conductive properties enable columnar LCs to be applied for optoelectric materials, such as thin-film transistors and photovoltaics.^[2] In general, columnar LC phases are formed by the self-assembly of discotic molecules consisting of a "flat" aromatic core and flexible peripheral chains, and their packing symmetries are determined by the shape of the constituent columns.^[3] Although most columnar LCs rely on the classical flat discotic mesogens, some exceptional examples based on nonplanar cores such as dendritic,^[4] bowl-like,^[5] tetrahedral,^[6] and octahedral^[7] shapes have been reported to reveal columnar LC phases. In several cases, three-dimensional (3D) aromatic stacks are formed within a column, which showed interesting material functions, for example, ferroelectric properties.[8]

[a]	J. Kim, Prof. BK. Cho
	Department of Chemistry, Dankook University
	Jukjeon 126, Gyeonggi, 448-701 (Korea)
	Fax: (+ 82) 31-8005-3153
	E-mail: chobk@dankook.ac.kr
[b]	Prof. S. Cho
	Department of Chemistry
	Chonnam National University
	Gwangju, 500-757 (Korea)
	Supporting information for this article is available on the WWW under

http://dx.doi.ora/10.1002/chem.201403297.

Some aromatic materials exhibit strongly emissive phenomena in the aggregation or bulk states, which is referred to as aggregation-induced emission (AIE).^[9] Many AIE-active materials can switch their luminescent color in response to external stimuli such as temperature, pressure, and vapor, which accompanies a morphological variation. LC molecules have been used to manufacture stimuli-responsive luminescent materials. To date, some thermochromic materials have been reported to reveal their fluorescence color change based on LC-to-liquid transitions, but the number is still limited.^[10]

The frustration of the molecular shape guideline for columnar LCs can be achieved in an LC system with propeller-like mesogens. Tetraphenylethylene (TPE) is an interesting mesogenic candidate because it is not only an ideal rigid propeller in molecular shape but also has a unique AIE property.^[11] To date, several research groups have reported a few LC examples containing TPE moieties.^[12] However, the intrinsic packing and emission properties of propeller-like TPE mesogens in "columnar LC phases" are not precisely understood. In this context, we intuitively thought that the stacking structures of propeller-like mesogens, including TPE derivatives, would be fundamentally distinct from classical planar discotic LCs. Considering the 3D propeller-like shape, some degree of the interdigitation between adjacent aromatic wings could be expected and modulated by the variation of molecular design. Therefore, it is worth investigating the assembling and photophysical behavior of TPE-based LCs in order to understand propeller LC systems.

To this end, we prepared TPE-based propeller-like molecules 1 and 2 (Figure 1 a). In the molecular design, the 1,2,3-triazolyl group was incorporated as a linkage group between the TPE and benzenyl groups by click chemistry.^[13] We considered that the polar character of the triazolyl group may reinforce microphase separation, which produces stable LC phases.^[14] Indeed, in comparison to TPE-based LC analogues with ether or ester linkages, $^{[12a,b]}$ the isotropic transition temperatures of 1 and 2 are more than 80 °C higher. To manipulate the packing structure of the propeller-like mesogens, the number of peripheral dodecyl chains was changed from eight (1) to twelve (2), because the space-filling of alkyl chains could influence the stacking of propeller mesogens.

Molecular propellers 1 and 2 were synthesized, as outlined in Scheme S1 (see the Supporting Information). The TPE precursor with four ethynyl units, 1,1,2,2-tetrakis(4-ethynylphenyl)ethene (A), was prepared by a reaction sequence from a Sonogashira reaction to McMurry coupling.^[15] The aromatic

Chem. Eur. J. 2014, 20, 12734 - 12739

Wiley Online Library



Colhex Colrec Co

cates the torsional variation by the rotation of the phenyl rotor. Temperatures are given in °C. The values in parentheses are the enthalpy change ($kJ mol^{-1}$) of each transition. Optical textures of (b) 1 at 181°C, (c) 1 at 159°C, and (d) 2 at 131°C. Col_{rec}, rectangular columnar; Col_{nex}, hexagonal columnar; I, isotropic liquid phase.

azide precursors (**1-azide** and **2-azide**) were prepared by etherification, and/or nitration, reduction, and azidation reac-

tions.^[16] The final click reactions were performed by using $CuSO_4$ ·5 H₂O and sodium ascorbate as reagents, producing the target molecular propellers (**1** and **2**). All experimental data fitted well with the designed molecular structures (see the Supporting Information).

The thermal properties of molecular propellers were analyzed by differential scanning calorimetry (DSC) at a rate of 10°C min⁻¹ (Figure S3, see the Supporting Information). Molecule 1, with eight dodecyl chains, exhibited two first-order transitions at 173.4°C and 186°C on the heating scan, which were observed to be reversible on the cooling scan. The small degrees of supercooling ($\Delta T < 5^{\circ}$ C) for both phase transitions in the DSC data suggest the existence of two different LC phases with temperature. This thermal behavior was also examined by polarized optical microscopy (POM). On cooling from the isotropic liquid phase, the LC phase at 181°C displayed a fan-like texture, which is typically found in the columnar LC phase of discotic LCs (Figure 1 b).^[17] On further cooling to the other LC phase at 159°C, the fan-like texture did not alter, instead persisting to room temperature (Figure 1 c). Only the texture color changed, which is due to some variations in the sample thickness as the temperature decreased. This POM data implies that there is significant structural change with the LC-to-LC transition of 1.

In contrast to 1, molecule 2, with twelve dodecyl chains, showed only an LC phase. In the DSC data, an endothermic peak was observed at 139.4 °C on heating and it also appeared on cooling. Like 1, the POM texture of this LC phase displayed a fan-like texture, which indicates the formation of a columnar phase

weak reflections, with *q*-spacing ratios of $1:\sqrt{3}:\sqrt{4}$ (Figure 2a), which could be indexed as the (10), (11), and (20) planes of

CHEMISTRY

(Figure 1 d). Consequently, mo-

lecular propellers **1** and **2** formed stable LC phases over

wide temperature ranges of RT

to more than 130°C. These LC

temperature windows mean en-

hanced microphase segregation between the aromatic mesogens

To characterize the microstructures, we performed temperature-variable small and wide angle X-ray scattering (SAXS and

tions (Figures 3 c and S4 in the

Supporting Information). The

SAXS pattern of **1** at 180 °C showed one strong and two

and dodecyl chains.^[18]

uropean Journal

Communication



Figure 2. (a) SAXS data at various temperatures, (b) the 2D SAXS data from the surfacealigned sample at 30 °C, (c) the unit cells (blue lines) of the Col_{rec} and Col_{hex} phases of 1, (d) models of "tilt" and "zigzag" stackings, (e) the molecular organization in the zigzag stacking of the Col_{rec} phase of 1, and (f) the schematics for the variation in the degree of interdigitation between propeller-like mesogens at the intercolumnar transition.



a two-dimensional (2D) hexagonal structure (Colhex) with the intercolumnar distance (a) of 3.86 nm. On cooling to 170°C, several new reflections appeared, together with the three reflections in the Col_{hex} (Figure 2 a). For further analysis, 2D SAXS measurements with surface-aligned samples were conducted. The aligned samples were made by casting the chloroform solution of 1 (~8 wt%) on 3-aminopropyltriethoxysilane (APS)coated Si wafers, and were slowly cooled from the liquid phase. Owing to the hydrophobic nature of the APS-coated surface, the columns aligned parallel to the substrate. The 2D SAXS data revealed many spot-like reflections, which could be assigned as the lattice planes of a 2D primitive rectangular structure in a multi-domain sample with four distinct orientations (Figure 2b and Table S1 in the Supporting Information). The lattice constants were determined to be a = 6.95 nm and b = 3.87 nm (a > b; Figure 2 c).

Similar intercolumnar transitions from a rectangular to hexagonal lattice have been observed in a few discotic and polycatenar LCs.^[19] In these previous cases, the transition occurred by the tilting of rigid cores along the column axis (Figure 2 d). According to the tilt mechanism, the primary d spacing of the rectangular phase should be smaller than that of the hexagonal phase at the transition. However, the (10) reflection of the Colhex phase of 1 divided into the (11) and (20) reflections of the Col_{rec} phase by keeping the dimension nearly constant (Figure 2a). This suggests that the transition of 1 does not conform to the tilt mechanism. The deviation from the tilt mechanism can be corroborated by examining the columnar crosssectional area (S) calculated from the SAXS data. The S value of Col_{rec} was calculated to be 1345 Å², which is even greater than that of Col_{hex} (1289 Å²; Table S2 in the Supporting Information). Therefore, from these X-ray analyses, we conclude that the intercolumnar transition of 1 is not driven by the known "tilt" mechanism. Instead, a translational displacement of aromatic propellers, referred to as "zigzag" stacking, can be proposed as a plausible mechanism (Figure 2 d). In the Col_{hex} phase, propeller mesogens stack orthogonally on top of each other. In this situation, the mesogens rotate along the column axis to form the circular cross section (Figure 2c). In contrast, to cover the expanded columnar area, the aromatic cores of the Col_{rec} phase should stack up in a zigzag manner (Figure 2e).

This unusual rearrangement of the aromatic cores at the intercolumnar transition of 1 can be understood in terms of the mesogenic structure. In contrast to conventional "flat" discogens, the TPE-based mesogen has a propeller-like structure. To fill the columnar space efficiently, the molecules should interdigitate to some extent on top of each other (Figure 2 f). This could be rationalized by checking the number of molecules (N) in a columnar cross section. The N value can be obtained by dividing the volume (V_{cs}) of a columnar cross section by the molecular volume (V_{mol}). The density ($\rho = 0.861 \text{ g cm}^{-3}$) of 1 measured at RT was employed for the calculation of both the Col_{rec} and Col_{hex} phases. Assuming that the thickness (h) of a columnar cross section is equal to the mean distance of liquid-like alkyl chains, the h values were obtained from the maxima of the halo signals in the WAXS data (Table S2 and Figure S4 in the Supporting Information). The N values for the Col_{rec} and Col_{hex} phases were calculated to be 1.31 and 1.33, respectively (Table S2 in the Supporting Information). As the calculation for Col_{hex} used the identical ρ value, the *N* value for Col_{hex} may be slightly overestimated. These non-unit values indicate that wings of aromatic propellers stack in an interdigitated mode (Figure 2 f).

Along with this interdigitated stacking, another factor should be considered to understand the intercolumnar transition from Col_{hex} to Col_{rec} . Taking into account the anisotropic rectangular symmetry of the Col_{rec} phase, the rotational motions of propeller-like mesogens along the column axis are more restricted in Col_{rec} than Col_{hex} (Figure 2e). To gain a clue as to the difference in the rotational barriers between the two LC phases, the core distance $(h_{core} = h/N)$, which is defined as the distance between neighboring TPE ethylenic groups, was calculated by dividing the thickness (h) of a columnar cross section by the number of molecules (N) in a columnar cross section. The $h_{\rm core}$ values were found to be 3.40 and 3.56 Å for Col_{rec} and Col_{hex} , respectively (Table S2). In contrast to the N value, the h_{core} (3.56 Å) of Col_{hex} may be slightly underestimated. The smaller $h_{\rm core}$ value of ${\rm Col}_{\rm rec}$ means that propeller-like mesogens are closer at the intercolumnar transition (Figure 2 f). Therefore, the aromatic wings are more strongly interdigitated, which hinders the rotational motions of mesogens, leading to an anisotropic aromatic cross section with a zigzag stacking in Col_{rec}.

The proposed zigzag stacking model with the smaller $h_{\rm core}$ value may agree well with the first-order character of the Col_{rec}-to-Col_{hex} transition in the DSC results because of the compact zigzag packing (Figure S3 in the Supporting Information). The compact zigzag packing can increase the degree of mesogenic interaction in comparison to the loose packing in the Col_{hex} phase. Notably, this first-order transition is an unusual phenomenon. To date, symmetry-breaking columnar LC transformations revealed a second-order character because their tilting mechanism of "flat" discogens does not require a significant change in the mesogenic interaction.^[20]

Molecular propeller 2 revealed a columnar phase. Like with the Col_{hex} phase of 1, the SAXS data at 30° C exhibited a 2D hexagonal lattice with the lattice parameter (a) of 3.92 nm (Figure 3a and Table S1 in the Supporting Information). This lattice parameter is similar to that of the Col_{hex} of 1 (3.86 nm), although the number of dodecyl chains has been increased from eight to twelve. From this, it can be speculated that the increased alkyl peripheries contribute to the expansion of the intercore distance owing to the elevated in-plane steric repulsion by the bulky alkyl peripheries of **2**. Indeed, the h_{core} value of the Col_{hex} phase of **2** was calculated to be 4.01 Å, which is larger than that of 1 (Figure 3b and Table S2). For 2, 2D X-ray diffraction data from a surface-aligned sample was obtained (Figure 3 c). In the small angle region, arced reflections corresponding to the hexagonal symmetry were observed, consistent with the 1D SAXS result. On the other hand, the WAXS data showed two broad isotropic reflections. An intense reflection at a larger q spacing of 14.2 nm⁻¹ is a typical halo signal, indicating the mean distance (h = 4.43 Å) of liquid-like alkyl chains. Additionally, a less intense halo signal appeared near



Figure 3. (a) SAXS data, (b) the schematic of the intercore distance, (c) the 2D WAXS data at 30 $^{\circ}$ C, (d) the vertical cut of the 2D WAXS data, and (e) the packing structure in the Col_{hex} phase of **2.** In (c), the spots in the small-angle region represent the reflections from the hexagonal symmetry.

the *q* spacing of 8.0 nm⁻¹ (Figure 3 c and d). Its *d* spacing is approximately 8.0 Å, which is nearly twice the distance of the h_{core} of 4.01 Å. From this, it can be said that aromatic mesogens stack with a mutual rotating angle between adjacent molecules of 90° (Figure 3 e), which leads to efficient space filling of the C_2 -symmetric **2**.^[21]

The thermochromic properties were examined under 365 nm UV light upon heating. Both molecular propellers displayed emission color variation

with temperature. Among them, a sudden fluorescence color change was observed at the intercolumnar transition of 1. As shown in Figure 4a, the emission color is sky blue for the Col_{rec} phase, which changed to emerald at the transition temperature of 170°C. Finally, the Colhex phase displayed a green color. The green emission persisted in the liquid phase but became dimmer as the temperature increased. For molecular propeller 2, on the other hand, the emission color change from sky blue to green occurred continuously in the Colhex phase (Figure S5 in the Supporting Information).

To obtain more information about the fluorescence behavior, time-resolved fluorescence measurements for 1 and 2 were performed. As shown in Figure 4b, the narrow emission bands at 475 nm for 1 and 2 rapidly disappeared and broad emission bands around 530 nm survived for a long time, indicating that there are at least two emissive states in 1 and 2. These trends are consistent with the short fluorescence lifetime of 0.85 or 1.37 ns at 450 nm and the relatively long lifetime of 2.94 or 3.81 ns at 555 nm for 1 and 2, respectively (Figure S6 in the Supporting Information). These spectroscopic results indicate that there are two kinds of distinct local environments caused by the structural heterogeneity of **1** and **2**. As the π conjugation length is a major factor to determine the emission wavelength of 1 and 2, we suggest that the narrow blue-edge emission with a shorter fluores-

cence lifetime mainly originates from a local environment with a shorter π -conjugation length and that the broad emission around 530 nm with a longer fluorescence lifetime is due to a different local environment with a longer π -conjugation length.

In addition, we examined the temperature dependency of the emission bands with short and long wavelengths (Figure 4 c). For **1**, the intensity of the band at 475 nm continu-



Figure 4. (a) Emission color change of 1 as a function of temperature under 365 nm UV light at a heating rate of 10° C min⁻¹. (b) Transient emission spectra at 25 °C at several time delays from 0 to 7 ns, and (c) the normalized fluorescence intensity change of two emission bands at 475 nm (450 nm) and 575 nm (555 nm) of 1 (2) as a function of temperature after photoexcitation at 375 nm.

www.chemeurj.org



ously decreased on going from the LC to the liquid phase. On the other hand, the band at 575 nm for 1 became weakened in the Col_{rec} phase but became stronger upon entering the Col_{hex} phase. This result means that the relative contribution of the more conjugated component is significant in Col_{hex} . In contrast to 1, the intensities of both bands at 450 nm and 555 nm for 2 simultaneously decreased upon heating, although the band at the longer wavelength decreased more gradually. These observed spectroscopic data are identical to the emission color change. During the LC transition to Col_{hex} in 1, the contribution of the more conjugated component considerably increases, resulting in the sudden bathochromic shift to green.

Based on the structural analysis of 1 and 2 and several previous studies about crystalline TPEs and dibenzofulvenes, the emission color change is associated with the conformational variation of the propeller-like aromatic mesogen.^[22] In the Col_{rec} phase of 1, the rotational motions of the aromatic wings are significantly hindered owing to the smaller intercore distance (Figure 2 f). This may lead to the greater twist angle with respect to the ethylenic stator, by which the π -conjugation length reduces, resulting in the sky-blue emission. However, after the transition into the Colhex phase upon heating, the rotational motions of the aromatic wings with respect to the ethylenic stator become vigorous. This thermal transition produces more planar conformations of the propeller mesogens. The conformational difference at the intercolumnar transition distinguishes the fluorescence color between Col_{rec} and Col_{hex} of 1. In contrast to 1, the conformational freedom of 2 does not increase discontinuously, but continuously upon heating because the rotations of the aromatic wings are not strictly hindered in the Colhex phase. Consequently, a continuous change in emission color was observed in the Col_{hex} phase of **2**.

It should be noted that the emission color variation of 1 occurred reversibly. Indeed, the emission color and spectra recorded during the heating process could be observed during the cooling process (Figure S7 in the Supporting Information). In some color-tunable luminogens reported previously, complex processes such as grinding-fuming, grinding-annealing, or long-time annealing, are required because their mechanisms are based on crystal-to-amorphous or crystal-to-crystal transitions.^[23] In contrast, the emission color of 1 is modulated simply by temperature. The thermochromic behavior of 1 must come from the nature of the LC materials. It is because the molecular reorganization is much faster for LC-to-LC transitions than crystal-to-amorphous transitions, as recognized by the small degree of supercooling in the DSC data.

In conclusion, we verified the unusual intercolumnar transformation and the packing dependency of the fluorescence property in the propeller-like LC system. In contrast to "second-order" Col_{rec} -to- Col_{hex} transitions in discotic or polycatenar LCs, the intercolumnar transition of **1** was "first order", which is due to the difference in degree of interdigitation of 3D aromatic propellers. Moreover, the intercolumnar LC transition led to the sudden change in emission color. So far, only a thermochromic case has been reported, which is based on a LC-to-LC phase transition (smectic-to-smectic phase transition).^[24] Therefore, the fluorescent thermochromism of molecu-

lar propeller **1** is a unique example because it is based on the intercolumnar LC phase transition. The propeller-like LC approach suggested in this study would be useful for the development of stimuli-responsive functional materials.

Acknowledgements

This work was supported by the National Research Foundation (NRF) of Korea grant funded by the Ministry of Education, Science and Technology (MEST), Republic of Korea (No. 2012R1A2A2A01045017). We acknowledge the Pohang Accelerator Laboratory (Beamline 9A), Korea.

Keywords: click chemistry · fluorescence · liquid crystals · liquid crystalline propeller · propeller mesogen · thermochromism

- a) D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etzbachi, H. Ringsdorf, D. Haarer, *Nature* **1994**, *371*, 141–143; b) X. Feng, V. Marcon, W. Pisula, M. R. Hansen, J. Kirkpatrick, F. Grozema, D. Andrienko, K. Kremer, K. Müllen, *Nat. Mater.* **2009**, *8*, 421–426; c) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902–1929; d) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson, H. Duan, *Nature* **2002**, *417*, 384–387.
- [2] C. D. Simpson, J. Wu, M. D. Watson, K. Müllen, J. Mater. Chem. 2004, 14, 494–504.
- [3] a) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem.* 2007, *119*, 4916–4973; *Angew. Chem. Int. Ed.* 2007, *46*, 4832–4887; b) S. Kumar, *Chem. Soc. Rev.* 2006, *35*, 83–109; c) R. J. Bushby, O. R. Lozman, *Curr. Opin. Colloid Interface Sci.* 2002, *7*, 343–354.
- [4] a) B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam, V. Percec, *Chem. Rev.* **2009**, *109*, 6275–6540; b) D. Miyajima, F, Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata, T. Aida, *J. Am. Chem. Soc.* **2010**, *132*, 8530–8531.
- [5] a) B. Xu, T. M. Swager, J. Am. Chem. Soc. 1993, 115, 1159–1160; b) Y. Matsuo, A. Muramatsu, Y. Kamikawa, T. Kato, E. Nakamura, J. Am. Chem. Soc. 2006, 128, 9586–9587; c) T. Hatano, T. Kato, Chem. Commun. 2006, 1277–1279; d) V. Percec, M. R. Imam, D. A. Wilson, P. A. Heiney, J. Am. Chem. Soc. 2009, 131, 1294–1304; e) K. Sato, Y. Itoh, T. Aida, J. Am. Chem. Soc. 2011, 133, 13767–13769.
- [6] a) A. Pegenau, P. Göring, C. Tschierske, *Chem. Commun.* 1996, 2563–2564; b) A. Pegenau, T. Hegmann, C. Tschierske, S. Diele, *Chem. Eur. J.* 1999, 5, 1643–1660; c) X. H. Cheng, S. Diele, C. Tschierske, *Angew. Chem.* 2000, 112, 605–608; *Angew. Chem. Int. Ed.* 2000, 39, 592–595; d) E. Cavero, S. Uriel, P. Romero, J. L. Serrano, R. Giménez, *J. Am. Chem. Soc.* 2007, 129, 11608–11618.
- [7] a) H. Zheng, T. M. Swager, J. Am. Chem. Soc. 1994, 116, 761–762; b) S. T. Trzaska, H.-F. Hsu, T. M. Swager, J. Am. Chem. Soc. 1999, 121, 4518–4519.
- [8] a) D. Guillon in Advances in Chemical Physics, Vol. 113 (Eds.: I. Prigogine, S. A. Rice, J. K. Vij), Wiley, Hoboken, **2007**, pp. 1–49; b) M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato, E. Nakamura, Nature **2002**, 419, 702– 705.
- [9] a) Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.* 2011, 40, 5361–5388;
 b) J. Wu, W. Liu, J. Ge, H. Zhang, P. Wang, *Chem. Soc. Rev.* 2011, 40, 3483–3495.
- [10] a) F. Camerel, L. Bonardi, M. Schmutz, R. Ziessel, J. Am. Chem. Soc. 2006, 128, 4548–4549; b) A. Hayer, V. de Halleux, A. Köhler, A. El-Garoughy, E. W. Meijer, J. Barberá, J. Tant, J. Levin, M. Lehmann, J. Gierschner, J. Cornil, Y. H. Geerts, J. Phys. Chem. B 2006, 110, 7653–7659; c) Y. Sagara, T. Kato, Angew. Chem. 2008, 120, 5253–5256; Angew. Chem. Int. Ed. 2008, 47, 5175–5178; d) Y. Sagara, T. Kato, Nat. Chem. 2009, 1, 605–610; e) V. N. Kozhevnikov, B. Donnio, D. W. Bruce, Angew. Chem. 2008, 120, 6382–6385; Angew. Chem. Int. Ed. 2008, 47, 6286–6289; f) F.

Würthner, *Chem. Commun.* **2004**, 1564–1579; g) S.-J. Yoon, J. H. Kim, K. S. Kim, J. W. Chung, B. Heinrich, F. Mathevet, P. Kim, B. Donnio, A.-J. Attias, D. Kim, S. Y. Park, *Adv. Funct. Mater.* **2012**, *22*, 61–69.

- [11] Z. Zhao, J. W. Y. Lam, B. Z. Tang, J. Mater. Chem. 2012, 22, 23726–23740.
- [12] a) A. Schultz, S. Diele, S. Laschat, M. Nimtz, Adv. Funct. Mater. 2001, 11, 441–446; b) A. Schultz, S. Laschat, S. Diele, M. Nimtz, Eur. J. Org. Chem. 2003, 2829–2839; c) Z. Yuan, Z.-Q. Yu, P. Lu, C. Deng, J. W. Y. Lam, Z. Wang, E.-Q. Chen, Y. Ma, B. Z. Tang, J. Mater. Chem. 2012, 22, 3323; d) W.-H. Yu, C. Chen, P. Hu, B.-Q. Wang, C. Redshaw, K.-Q. Zhao, RSC Adv. 2013, 3, 14099–14105.
- [13] a) M.-H. Ryu, J.-W. Choi, B.-K. Cho, J. Mater. Chem. 2010, 20, 1806–1810;
 b) B.-K. Cho, Polym. J. 2012, 44, 475–489.
- [14] B.-K. Cho, S.-H. Kim, Soft Matter 2014, 10, 553.
- [15] N. B. Shustova, A. F. Cozzolino, M. Dinca, J. Am. Chem. Soc. 2012, 134, 19596–19599.
- [16] E. Beltrán, J. L. Serrano, T. Sierra, R. Giménez, Org. Lett. 2010, 12, 1404– 1407.
- [17] M.-H. Ryu, J.-W. Choi, H.-J. Kim, N. Park, B.-K. Cho, Angew. Chem. 2011, 123, 5855 – 5858; Angew. Chem. Int. Ed. 2011, 50, 5737 – 5740.
- [18] C. Tschierske, J. Mater. Chem. 1998, 8, 1485-1508.
- [19] a) A. M. Levelut, J. Chim. Phys. Phys.-Chim. Biol. 1983, 80, 149–161;
 b) C. R. Safinya, K. S. Liang, W. A. Varady, N. A. Clark, G. Andersson, Phys. Rev. Lett. 1984, 53, 1172–1175; c) A. C. Ribeiro, B. Heinrich, C. Cruz, H. T. Nguyen, S. Diele, M. W. Schröder, D. Guillon, Eur. Phys. J. E 2003, 10, 143–151; d) B. Donnio, B. Heinrich, H. Allouchi, J. Kain, S. Diele, D. Guillon, D. W. Bruce, J. Am. Chem. Soc. 2004, 126, 15258–15268.

- [20] a) M. Lehmann, G. Kestemont, R. G. Aspe, C. Buess-Herman, M. H. J. Koch, M. G. Debije, J. Piris, M. P. de Hass, J. M. Warman, M. D. Watson, V. Lemaur, J. Cornil, Y. H. Geerts, R. Gearba, D. A. Ivanov, *Chem. Eur. J.* 2005, *11*, 3349–3362; b) N. Spielberg, M. Sakar, Z. Luz, R. Poupko, J. Billard, H. Zimmermann, *Liq. Cryst.* 1993, *15*, 311–330.
- [21] R. Perochon, P. Davidson, S. Rouziére, F. Camerel, L. Piekara-Sady, T. Guizouarn, M. Fourmigue, J. Mater. Chem. 2011, 21, 1416-1422.
- [22] a) R. Hu, J. W. Y. Lam, Y. Liu, X. Zhang, B. Z. Tang, *Chem. Eur. J.* 2013, *19*, 5617–5624; b) X. Zhang, Z. Chi, H. Li, B. Xu, X. Li, W. Zhou, S. Liu, Y. Zhang, J. Xu, *Chem. Asian J.* 2011, *6*, 808–811; c) Y. Dong, J. W. Y. Lam, A. Qin, Z. Li, J. Sun, H. H.-Y. Sung, I. D. Williams, B. Z. Tang, *Chem. Commun.* 2007, 40–42.
- [23] a) X. Luo, J. Li, C. Li, L. Heng, Y. Q. Dong, Z. Liu, Z. Bo, B. Z. Tang, Adv. Mater. 2011, 23, 3261–3265; b) B. Xu, Z. Chi, J. Zhang, X. Zhang, H. Li, X. Li, S. Liu, Y. Zhang, J. Xu, Chem. Asian J. 2011, 6, 1470–1478; c) X. Gu, J. Yao, G. Zhang, Y. Yan, C. Zhang, Q. Peng, Q. Liao, Y. Wu, Z. Xu, Y. Zhao, H. Fu, D. Zhang, Adv. Funct. Mater. 2012, 22, 4862–4872; d) Y. Abe, S. Karasawa, N. Koga, Chem. Eur. J. 2012, 18, 15038–15048; e) J. Shi, W. Zhao, C. Li, Z. Liu, Z. Bo, Y. Dong, Y. Dong, B. Z. Tang, Chin. Sci. Bull. 2013, 58, 2723–2727.
- [24] S. Yamane, Y. Sagara, T. Kato, Chem. Commun. 2009, 3597-3599.

Received: April 28, 2014 Published online on August 14, 2014